

Fermiology and transport properties of the half-metallic itinerant ferromagnet CoS_2 : influence of spin orbit coupling

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Electronic structure calculations were performed on the compound CoS_2 , an itinerant ferromagnet whose magnetic properties can be understood in terms of spin fluctuation theory. We have identified nesting features in the Fermi surface of the compound, active for long wavelength spin fluctuations. The electronic structure of the material is close to a half-metal. We show the importance of introducing spin-orbit coupling (SOC) in the calculations, that partially destroys the half-metallicity of the material. By means of transport properties calculations, we have quantified the influence of SOC in the conductivity at room temperature, with an important decrease comparing to the GGA alone conductivity. SOC also helps to understand the negative ρ of the material, whose conductivity varies by a few percent with the introduction of small perturbations in the states around the Fermi level.

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I. INTRODUCTION

Half metals^{1,2} are materials where metallic conduction occurs only through one of the spin channels, leading to a perfectly polarized electron current. One of the spin channels presents a gap at the Fermi Energy (E_F) but the other one has bands crossing it. This makes them an interesting family of materials, in particular for applications in the field of spintronics,³ where spin injection is required for controlling the charge and spin currents separately. Moving a strongly spin-polarized current is highly sought for, and half-metals are a good candidate for this.

Several electronic structure calculations based on density-functional theory (DFT) have been done in the last few years, describing CoS_2 as a half-metallic ferromagnet.⁴⁻⁹ However, the electronic and magnetic properties of this material are not fully understood. Point-contact Andreev reflection measurements¹⁰ showed a relatively low-spin polarization of 56% at 4.2K.¹¹ This picture was confirmed in the studies by Wang *et al.*¹² in the $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$ series, where they show that the spin polarizations can be ρ tuned in the range $-56\% < P < +85\%$. Brown *et al.*¹³ found from polarized neutron-diffraction measurements that half metallicity does not occur in the ferromagnetic phase. A sharp photoemission peak at the Fermi energy in the ferromagnetic phase originates in the bottom of $e_{g\downarrow}$ subband due to the exchange 3 , indicating that the $e_{g\downarrow}$ band is partially filled in the ferromagnetic phase,¹⁴ destroying the half metallicity.

Recently it was found that the resistivity, spe-

cific heat and magnetic susceptibility of CoS_2 is dominated by exchange-enhanced spin-density fluctuations.¹⁵ This previous work also show that the GGA method¹⁶ is enough to describe the electronic and magnetic ρ of CoS_2 due to the non localized nature of the compound. There is no need to introduce strong correlation effects to describe accurately its electronic structure properties but not enough to describe the enhancement of, e.g. the value γ obtained from specific heat, which is enhanced due to spin fluctuations unaccounted for in DFT calculations.

The important role of spin-orbit coupling in a realistic description of half-metallic materials has been discussed in literature about half-metals.^{1,17} Usually the coupling between spin-up and spin-down states caused by a sizable spin-orbit coupling introduces non-negligible minority states at the Fermi level, destroying the half-metallicity. In general, this will depend on the strength of the interaction (that increases with atomic size) and also on the size of the gap and the position of the band edges in the insulating spin channel. The importance of minimizing the effects of spin-orbit coupling on destroying half-metallicity when designing new half-metals has been discussed in the past,¹⁸ where utilizing cations with completely filled shells was suggested in order to reduce the spin-orbit effects by minimizing the orbital angular momenta and, in the case of studying possible compensated half-metals, increasing the likelihood of the materials having no net magnetization.

However, most works based their studies solely on the changes in the density of states at the Fermi level, but the degree of half-metallicity will be influ-

enced by the changes in the conduction properties that derive from the reordering of states around the Fermi level introduced by spin-orbit coupling. Moreover, the conductivity of the minority spin channel will have an activated component that needs to be quantified beyond the value of the density of states at E_F . In this paper, we will make an analysis of the electronic and magnetic properties of the ground state of CoS_2 and introduce spin orbit coupling (SOC) to determine its importance in the half-metallicity of the material. We will also focus on explaining, from a band structure point of view, what features help us understand its behavior as an itinerant ferromagnet, governed by spin fluctuations. For analyzing the conduction properties of the material, its spin-dependence and the importance of spin-orbit coupling, we have made several transport properties calculations and have compared them with experimental measurements.

II. COMPUTATIONAL DETAILS

Electronic structure calculations were performed within density functional theory¹⁹ using WIEN2K software,^{20,21} which utilizes an augmented plane wave plus local orbitals (APW+lo)²² method to solve the Kohn-Sham equations. This method uses an all-electron, full-potential scheme that makes no shape approximation to the potential or the electron density. The exchange-correlation potential utilized was the Perdew, Burke and Ernzerhof (PBE) version of the general gradient 0 (GGA).¹⁶ The geometry optimization was carried out minimizing the forces in the atoms and the total energy of the system. The parameters of our calculations depend on the type of calculation but for any of them we converged with respect to the k -mesh and to $R_{mt}K_{max}$. Values used of the k -mesh are $7 \times 7 \times 7$ sampling of the full Brillouin zone for electronic structure calculations and geometry optimization, $40 \times 40 \times 40$ for the band structure calculations and the very fine details of the influence of spin orbit coupling in the half metallicity of the compound. $R_{mt}K_{max} = 6.0$ is chosen for all the calculations. Local orbitals were added for a bigger flexibility in dealing with the semicore states. Muffin tin radii chosen were the following: 2.31 a.u. for Co and 2.04 a.u. for S. All the calculations were converged with respect to all the parameters used, to the precision necessary to support our calculations (converged forces, total energy differences, etc.). For the calculations of transport properties we utilize the BoltzTraP code,²³ that uses the energy bands obtained from the WIEN2k software. We used a k -mesh in a $43 \times 43 \times 43$ sampling of the full Brillouin zone, where convergence was achieved. The calculation

of transport properties requires a fine mesh to carry out the integrations in the Brillouin zone. Spin orbit coupling (SOC) was introduced in a second-variational procedure.²⁴

III. STRUCTURE

CoS_2 crystallizes in a cubic pyrite structure,⁴ as shown schematically in Fig. 1. Co and S atoms are located respectively at the Wyckoff positions 4a (0,0,0) and 8c (u,u,u) of the space group $\text{Pa}\bar{3}$, no. 205. Co atoms are octahedrally coordinated by 6 S neighbors.

From X-ray diffraction experiments on large single crystals ($3 \times 3 \times 3 \text{ mm}^3$),¹⁵ we obtained the lattice parameter of the material to be $a = 5.518 \text{ \AA}$. Also, electronic structure calculations were performed to optimize *ab initio* the structural free parameter 0 the S position. This was calculated in order to minimize interatomic forces and the total energy of the system. The value obtained was $u = 0.387$ (see Table I), in good agreement with previous works.²⁵ Calculations to obtain the lattice parameter *ab initio* were performed yielding a lattice parameter $a = 5.55 \text{ \AA}$, which is within the typical accuracy of density functional theory calculations (2% in volume).

TABLE I: Crystallographic positions at $T = 0$ that result from our structure optimization.

Crystallographic		
Atom	position	Coordinates
Co	4a	(0,0,0)
S	8c	(0.387,0.387,0.387)

IV. RESULTS

A. Electronic structure and magnetism

The electronic structure of CoS_2 is characterized by a large covalency due to the extended S p bands overlapping largely the Co d bands close to the Fermi level. Also, the itineracy of the compound helps in making difficult to establish an ionic picture for the material. Some earlier reports suggest an effective $\text{Co}^{2+}:\text{d}^7$ state,⁷ distinct from the purely ionic picture.

Our results show that the orbital occupations are close to the $\text{Co}^{2+}:\text{d}^7$ state. As expected, a large covalency can be seen in the density of states (DOS) plots in Fig. 2. Big spectral weight from S p states appears near E_F and also significant weight can be

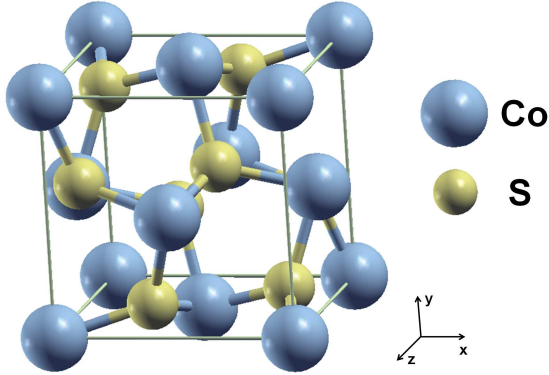


FIG. 1: (Color online) Cubic pyrite structure of the CoS₂ compound. Large blue spheres represent Co atoms and small yellow spheres represent S atoms.

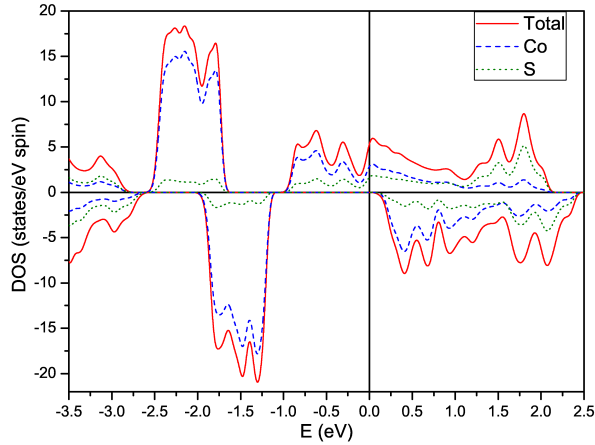


FIG. 2: (Color online) Spin-up (positive values) and spin-down (negative values) total density of states (DOS) plots for the CoS₂ in the ground state ferromagnetic configuration. Partial density of states have been plotted also (dash blue lines for Co total DOS and dot green lines for S total DOS). Fermi energy is at zero. The system is half-metallic.

seen at the top of the conduction bands, showing the S p bands are not fully occupied. In this DOS plot, calculated within the GGA approach, we see CoS₂ presents a half-metallic character, as noted in several previous works.^{7,26} It shows the fully occupied t_{2g} bands of about 0.7 eV bandwidth at about -1 to -2 eV, that are spin-split by about 0.6 eV, and the broad e_g^\uparrow bands crossing the Fermi level in the majority channel, being 2 eV wide. The e_g^\downarrow bands are unoccupied, with its edge lying very close to the Fermi level. This proximity will make their occupancy non-zero under perturbations such as spin-orbit coupling, temperature or the application of an

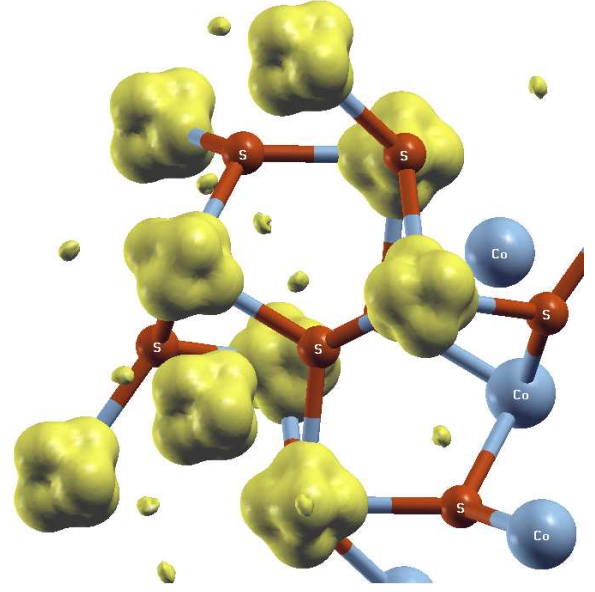


FIG. 3: (Color online) Charge difference of the majority and minority states of CoS₂ compound. Large blue spheres represent Co atoms and orange small spheres represent S atoms. The charge difference plotted correspond to an isosurface at $0.05 \text{ e}/\text{\AA}^3$ produced using XCrySDen.²⁷ The shape of the spin density isosurface represents the orbital that carries the spin moment, being a mixture of e_g states.

external magnetic field. A small amount of electron doping would also be able to populate them.

The value of the total moment obtained by ab initio calculations is $1.00 \mu_B/\text{Co}$ in the ground state ferromagnetic solution, in agreement with the value of the saturation magnetization found experimentally, of about $0.9 \mu_B/\text{Co}$.¹⁵ The moment comes from the partially filled majority e_g band. To illustrate this description of the electronic structure, we have produced a differential electron spin density plot (Fig. 3). This shows the difference in electronic density between the majority and minority states of the compound (yellow), in order to see the spatial distribution of the only unpaired electron (charge difference plot will show basically the density that corresponds to the e_g^\uparrow electron, because the t_{2g} bands are completely full). Charge accumulation can be seen along the Co-S direction (like $d_{3z^2-r^2}$ or $d_{x^2-y^2}$ in an octahedral environment). The large bandwidth of the e_g bands (about 2 eV), much higher than the crystal field splitting between the e_g sub-levels, leads to a similar occupation of both e_g orbitals, as we see in Fig. 3.

Our results show that a calculation at the GGA level is enough to capture the features of the electronic structure of this itinerant ferromagnet, as shown in a previous work.¹⁵ The introduction of

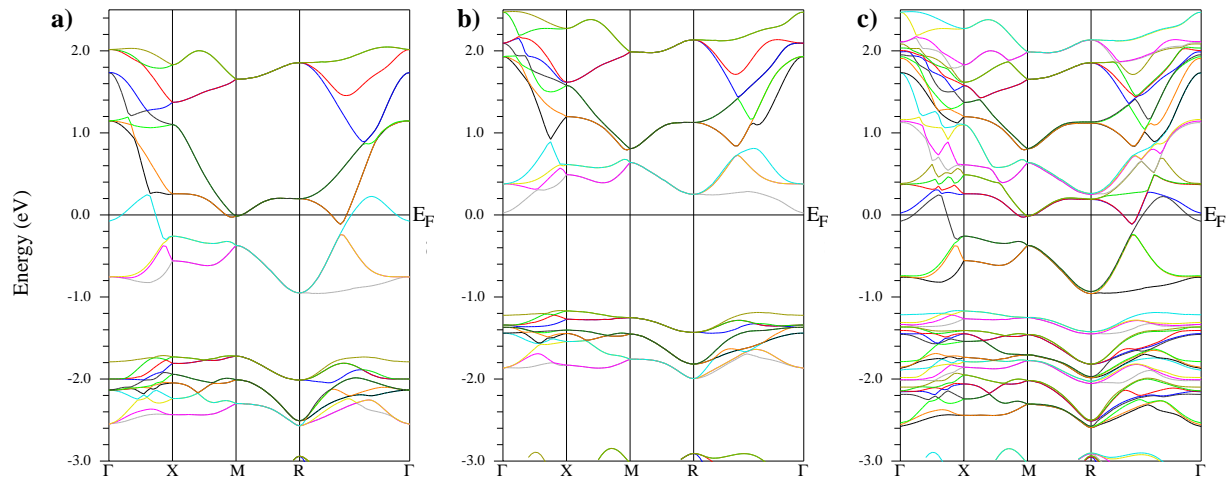


FIG. 4: (Color online) Band structure plot of the: a) majority spin states, b) minority spin states and c) calculation including spin orbit coupling with the magnetization along 001 direction. Observe that the curvature of the bands remains unaltered when spin-orbit coupling is turned on. Fermi level is at zero

strong correlation effects by the LSDA+U method²⁸ does not provide more information about the electronic structure of this itinerant system, in agreement with the work of Kwon *et al.*⁶ The correct ferromagnetic ground state is obtained at the GGA level (a FM solution is more stable by 75 meV/Co than the paramagnetic phase). A peak of the DOS at the Fermi energy (not shown) is found in a non-magnetic calculation, suggestive of the system being close to a ferromagnetic instability according to the Stoner criterion²⁹ ($N(E_F)I > 1$ to favor ferromagnetism).

Band structure plots (Fig. 4a and b for the majority and minority spin channel, respectively) can be used to understand the essential features of the electronic structure of CoS₂. Being a half-metal, all the spectral weight around the Fermi level comes from the majority spin channel (Fig. 4a). The minority spin channel (Fig. 4b) shows a gap of about 1 eV at the Fermi level. A big electron pocket, centered at the Γ point, and a large hole pocket appear in the Γ -R direction. Additional electron pockets appear near the M point. These results are similar to other band structure plots published using the GGA scheme,⁷ except for the electron pocket centered at the Γ point, which is absent in their calculations.

We have also performed calculations including SOC, with the magnetization along the main directions of the cubic structure: (001), (110) and (111). Calculations yield an orbital magnetic moment $0.037\mu_B$ (quenched by the crystal field³⁰), similar to that reported by Antonov *et al.*³¹ Together with the local spin magnetic moment of $0.92\mu_B$ (inside the Co muffin tin sphere) we obtain $M_l/M_s = 0.04$, i.e., $\langle l_z \rangle / \langle s_z \rangle = 0.08$, in good agreement

with experimental measurements (0.1).³²

A very small energy difference is obtained between the calculations with the magnetization along the three main directions of the crystal, suggesting a very small magnetocrystalline anisotropy in this largely isotropic material. The energy difference between the easy and hard axis is smaller than 50 $\mu\text{eV/Co atom}$.

Analyzing the band structure (Fig. 4c) obtained from a GGA+SOC (001) calculation, we observe that the introduction of SOC leads to small shifts in the bands, but the positions of the pockets in the Brillouin zone and the curvature of the bands remain roughly unchanged (we see all the electron and hole pockets discussed above). A splitting in the bands corresponding to the electron pocket in the Γ -R direction, and a variation in the size of the other pockets can be seen. Below we discuss further the quantitative effects in the electronic structure of introducing SOC.

For a better description of the states near the Fermi level, Fig. 5 shows the Fermi surface of the compound, within a GGA+SOC-based calculation with the magnetization set along the (001) direction. In the plot we observe a large isotropic electron pocket around the Γ point. Experimentally,¹⁵ the spin susceptibility of this compound can be understood in terms of spin fluctuation theory.³³ For this type of systems, peaks in the spin susceptibility can be associated to nesting features in the Fermi surface. In the case of CoS₂, some nesting features can be observed in the $\Gamma - M - R$ plane (Fig. 5 b)), with a nesting vector that we have denoted as Q_n . The magnitude of Q_n would correspond to long-wavelength spin fluctuations ($\lambda = 6a$, with a being

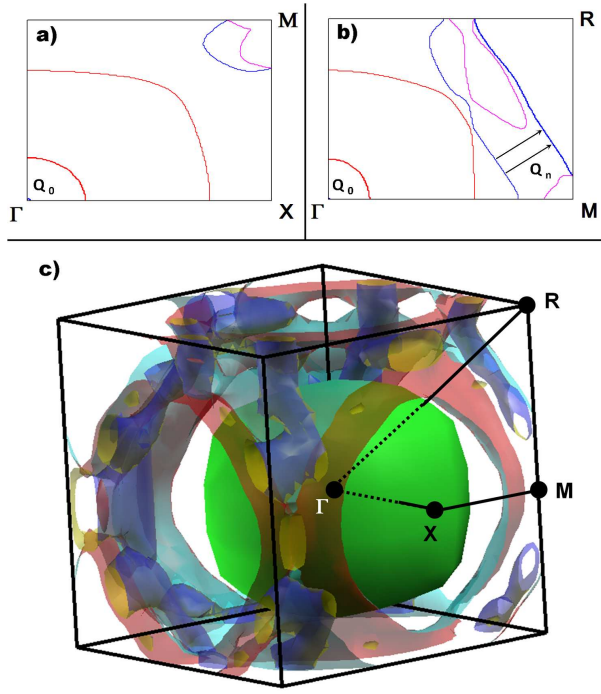


FIG. 5: (Color online) Fermi surface of the CoS_2 obtained for the majority spin channel in a FM solution, within a GGA+SOC-based calculation along the (001) direction. a) and b) show the 2-dimensional Fermi surface in the Γ -X-M and Γ -M-R planes, respectively. c) shows the 3-dimensional Fermi surface. In the inset b) we have denoted the nesting vector as Q_n (which corresponds to a wavelength of approximately 6 times the lattice parameter). This would lead to a peak in the spin susceptibility associated with that wave-vector, together with the ferromagnetic ones.

the lattice parameter), that are believed to exist in weak ferromagnets such as CoS_2 ¹⁵ and also MnSi ,³⁴ together with many other systems.³³ The rest of the Fermi surface, i.e. the hole pocket along Γ -R direction and the small electron pockets in the X-M direction near M, is largely incoherent and will lead to negligible nesting.

B. Half-metallicity

CoS_2 has been predicted to be a good source of spin polarized electrons;¹¹ hence, we will try to address this point with our calculations. GGA alone leads to half-metallic behavior (Fig. 2), as we saw above. Due to the proximity of the conduction band edge to the Fermi level in the minority spin channel, SOC destroys the half-metallicity noticeably, as we can see in Fig. 6. No minority DOS is seen in the GGA calculation, but magnifying the minority DOS

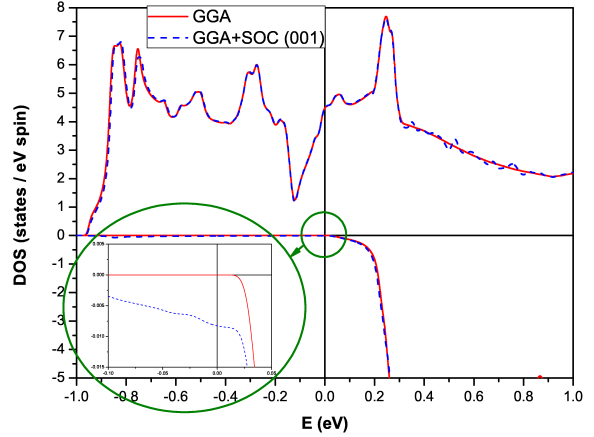


FIG. 6: (Color online) Spin-up (positive values) and spin-down (negative values) total DOS plots for the CoS_2 in the ferromagnetic configuration with a GGA (solid red line) and a GGA+SOC (SOC along (001) direction) (dash blue line). Fermi energy is at zero. The system is half-metallic in the GGA and 0 and 1 metallic in the GGA+SOC. The inset shows a zoom of the minority DOS near the 0 level of both solutions (GGA and GGA+SOC)

of the calculation including SOC (in the inset), we see the DOS is nonzero at the Fermi level for the minority spin channel. This has important consequences for the conduction properties of the material. We can compare the values of the DOS at the Fermi level for the two spin channels, being no longer infinite but $N(E_F)_\uparrow/N(E_F)_\downarrow = 540$ when SOC is considered, giving a polarization of the DOS at the Fermi level $P = [N_\uparrow(E_F) - N_\downarrow(E_F)]/[N_\uparrow(E_F) + N_\downarrow(E_F)]$ of 99.6%, very large still.

For analyzing further the degree of spin polarization of the carriers in this system, we have calculated the transport properties from our band structure calculations using a semiclassical 1 based on Boltzmann transport theory.²³ In order to understand the spin polarization of the carriers, it is necessary to go beyond the values of the DOS at the Fermi level. One possible way is to compare the conductivities of both spin channels. The inset of Fig. 7 shows the temperature dependence of the ratio between the subtraction and the sum of the conductivities coming from both spin channels, i.e. $P_\sigma = (\sigma_{up} - \sigma_{dn})/(\sigma_{up} + \sigma_{dn})$, defined analogously to that of the DOS. This quantity ranges from ± 1 for a full-polarization to 0 for no polarization and will give us the spin polarization of the carriers at a given temperature. When no SOC is considered and polarization of the DOS is infinite, it is still very large in terms of the conductivities (spin polarization of the carriers), being approximately $P_\sigma = 0.998$ at room temperature.

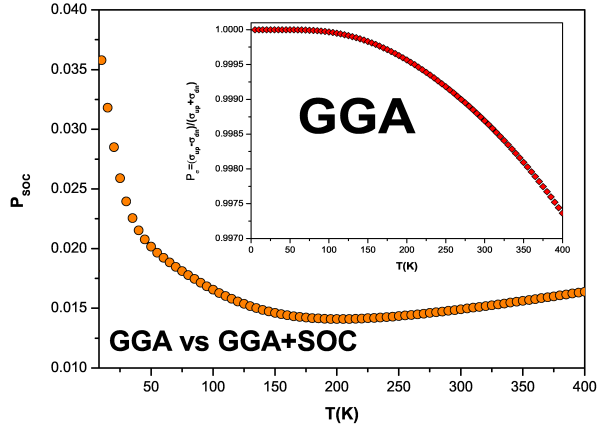


FIG. 7: (Color online) Percentage (P_{SOC}) of the better conduction of GGA versus GGA+SOC calculations. This is calculated by subtraction of the conductivities coming from GGA and GGA+SOC calculations, normalized to the sum of both them (solid orange circles) ($P_{SOC} = (\sigma_{nosoc} - \sigma_{soc}) / (\sigma_{nosoc} + \sigma_{soc})$). GGA alone leads better conduction properties, so the GGA+SOC implies larger resistivity. The inset show the 2 of the conductivities coming from both spin channels over the sum of these conductivities within the GGA 0 (solid red diamonds). At room temperature, σ_{up} contributes in a 99.8 % to the total conductivity and σ_{dn} 0.2 % contributes it to the total conductivity in the GGA 0.

One would naively expect that the introduction of SOC leads to a substantially larger conductivity coming from the minority spin channel compared to the case without SOC, because of the non-zero DOS at the Fermi level. To gain some insight on that, we present in Fig. 7 the temperature dependence of the calculated ratio between the subtraction and the addition of the conductivities calculated with and without SOC: $P_{SOC} = (\sigma_{nosoc} - \sigma_{soc}) / (\sigma_{nosoc} + \sigma_{soc})$. We observe that the solution without SOC has a larger conductivity than the solution including SOC up to room temperature, both values differing by about a few percent. Thus, the bigger change in the conductivity when introducing SOC in the calculations is not the additional contribution from the minority spin states, but an overall reduction in the conductivity. Even though a separation in conductivity from both spin channels is not possible when calculating with SOC, the results suggest a very large polarization of the carriers will still be present when the calculations include SOC. This effect will account for a reduction in the half-metallicity of just a few percent. However, to understand the experimental observations, one needs to consider other effects as possible sources against a full spin polarization, such as defects, spin excitations or non-quasiparticle states^{35,36} to be important.

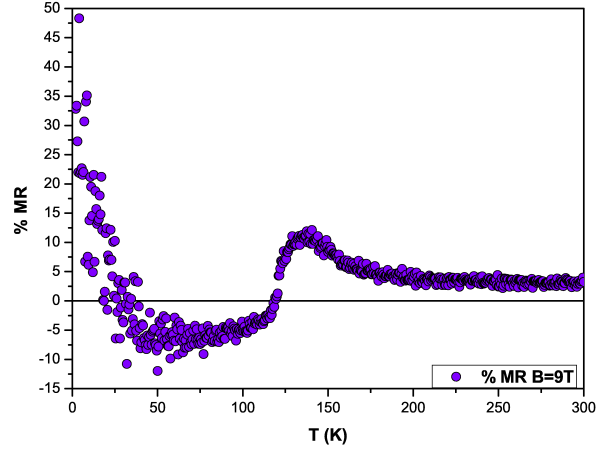


FIG. 8: (Color online) Evolution of the magnetoresistance with temperature measured comparing the values of resistivity at $H = 9T$ and $H = 0T$ applied magnetic field according to the formula $MR = 100(\rho_{9T} - \rho_{0T}) / \rho_{0T}$. Below 25K we observed positive MR, and negative MR are obtained in the rest of FM phase.

In a material with such a large polarization of carriers at the Fermi level, a negative magnetoresistance is expected to occur in the FM region of the phase diagram. Figure 8 shows the measurements of the magnetoresistance (MR) in an external magnetic field of 9 T, ($MR = 100(\rho_{9T} - \rho_{0T}) / \rho_{0T}$). These show a negative MR in a temperature range within the FM phase (below the Curie temperature $T_c = 122K$ ¹⁵) with a value ranging between -3% and -9%. At low temperatures, a large positive value of the MR is observed and, above the Curie point, in the paramagnetic phase, the MR becomes again positive, approaching a constant value of about 3% at high temperatures. MR does not reach a very high value, consistent with the fact that spin polarization of the carriers is not complete, as discussed above.

V. SUMMARY

We have analyzed the electronic structure and magnetic properties of this itinerant weak ferromagnet, dominated by spin-density fluctuations. We have related these to the nesting features in the Fermi surface associated to long wavelength nesting vectors. Being an itinerant system, the GGA scheme can describe its properties and electronic structure accurately, not needing to introduce the electron correlations with means of LDA+U. GGA calculations alone predict CoS_2 to be half metallic, but when introducing the important effects of SOC effects, the results of the calculations show SOC destroys the half-metallicity, non-zero occupa-

tion (band-crossing) of the minority channel at the Fermi level appear. Our transport properties calculations show that changes in the conductivity associated to the introduction of SOC in the calculations do not imply a significant break-up of the half-metallic behavior, but just a few percent. These results are consistent with our experimental observation of negative magnetoresistance in the material.

VI. ACKNOWLEDGMENTS

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